

XANTHONES FROM THREE *GARCINIA* SPECIES

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Key Word Index—*Garcinia nervosa*; *G. polyantha*; *G. pyrifera*; Guttiferae; 1,3,6,7-oxygenated xanthenes; 1,3,5,6-oxygenated xanthenes; chemotaxonomy.

Abstract—From the stem bark of three previously uninvestigated *Garcinia* species a number of xanthenes have been isolated including three that appear to be novel. The novel compounds are characterized as isocowanin (8-geranyl-4-(3,3-dimethylallyl)-7-methoxy-1,3,6-trihydroxyxanthone), isocowanol (8-geranyl-4-(3-hydroxymethyl-3-methylallyl)-7-methoxy-1,3,6-trihydroxyxanthone) and nervosaxanthone (4,8-di(3,3-dimethylallyl)-2-(1,1-dimethylallyl)-1,3,5,6-tetrahydroxyxanthone). The chemotaxonomic significance of oxygenation patterns in these xanthenes is briefly discussed.

INTRODUCTION

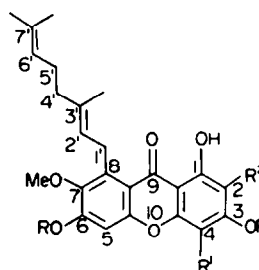
The genus *Garcinia* is widespread in the old World, most notably in the lowland tropical rain forests of south-east Asia and west Africa [1]. The genus has been the subject of a considerable amount of phytochemical investigation which has revealed it to be a major source of prenylated xanthenes and benzophenones and of biflavonoids linked between C-3 and C-8 [2]. In this paper we report the results of a study of the stem barks of three previously uninvestigated species, *G. nervosa* Miq., *G. pyrifera* Ridl., both collected in west Malaysia, and *G. polyantha* Oliv., collected in Cameroon. From each of the above xanthenes were obtained, three of the isolated compounds appearing to be novel. The findings are also discussed in the light of a recent paper [2] on the chemotaxonomy of *Garcinia* and allied genera of the Guttiferae, tribe Garcinieae.

RESULTS AND DISCUSSION

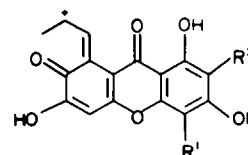
Garcinia pyrifera is a small tree of lowland forest distributed throughout the Malayan peninsula, Sumatra and Borneo [3]. Extraction of the stem bark with petrol and then ethyl acetate revealed identical mixtures which were bulked and subjected to column chromatography from which two triterpenes and three xanthenes were obtained. The former were identified as β -amyrin and oleanolic aldehyde.

The three xanthenes analysed for $C_{24}H_{26}O_6$, $C_{29}H_{34}O_6$ and $C_{29}H_{34}O_7$, and were identified as rubraxanthone (1), isocowanin (2) and isocowanol (3), respectively. The UV spectrum of 1 was typical of a 1,3,6,7-oxygenated xanthone and showed bathochromic shifts with $AlCl_3$ and $NaOAc$ indicative of free hydroxy groups at C-1 and at C-3 or C-6 [4, 5]. The 1H NMR spectrum revealed signals for an H-bonded hydroxy function

(δ 13.38) at C-1 and three aromatic protons as a *meta*-coupled AB quartet (δ 6.19 and 6.29) for H-2 and H-4 and a singlet at δ 6.81 (H-5). A single methoxy resonance occur-



- 1 $R = R' = R'' = H$
- 2 $R = R'' = H, R' = CH_2CH=C(Me)_2$
- 3 $R = R'' = H, R' = CH_2CH=C(Me)CH_2OH$
- 5 $R = Me, R' = CH_2CH=C(Me)_2, R'' = H$
- 6 $R = R' = H, R'' = CH_2CH=C(Me)_2$
- 7 $R = R' = H, R'' = CH_2CH=C(Me)CH_2OH$



4 [M - III]⁺

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red at $\delta 3.80$. The remaining non-replaceable protons appeared as a series of signals typical of a geranyl moiety, the most important feature being the deshielded position of the methylene group adjacent to the aromatic nucleus ($\delta 4.12$) indicating its location at C-8, *peri* to the carbonyl. The presence of a geranyl unit was confirmed by major ions at $[M - 69]^+$ and $[M - 123]^+$ in the mass spectrum while its placement at C-8 was indicated by $[M - 111]^+$ (4), a fragment typical of 8-geranyl-7-methoxy xanthenes [6]. The ^{13}C NMR spectrum (Table 1) was recorded for the first time and resonance positions assigned by comparison with data for other xanthenes [7]. It was particularly valuable in placing the methoxy group at C-7 due to its relatively deshielded resonance position (61.4 ppm) which required that both *ortho* positions be substituted. Rubraxanthone has previously been isolated from two other Asian species, *G. cowa* Roxb. [6] and *G. rubra* Merr. [8].

The ^1H NMR spectrum of 2 agreed with that for 1 except for the loss of one of the A-ring protons, leaving a singlet at $\delta 6.26$, and by additional signals for a 3,3-dimethylallyl unit. The continuing presence of the geranyl moiety at C-8 was confirmed from the mass spectrum (ion 4) and the methoxy group at C-7 by the ^{13}C NMR spectrum (Table 1). Placement of the additional prenyl

unit at C-4 was indicated by the ^{13}C NMR spectrum of the fully methylated derivative 5 (Table 1) in which three of the methyl resonances were shielded and one deshielded. By contrast placement of the prenyl unit at C-2 would have led to deshielding of two of the methyl resonances, those for C-1 and C-7. On this basis the xanthone must be assigned structure 2. It has been given the trivial name of isocowanin since it is isomeric with the known xanthone cowanin (6) reported from *G. cowa* [9].

Isocowanol (3) gave ^1H NMR data identical to 2 except for the loss of one methyl resonance and its replacement by a broad singlet (2H) at $\delta 4.40$, indicative of a hydroxymethyl group and therefore accounting for the additional oxygen in the empirical formula. The hydroxymethyl group was located in the A-ring prenyl substituent by the continued occurrence of the ion 4 as a feature of the mass spectrum. Once again the ^{13}C NMR spectrum of the fully methylated derivative (Table 1) established that the prenyl unit was at C-4, not C-2. Accordingly 3 has been assigned the trivial name isocowanol and is also isomeric with a xanthone from *G. cowa*, in this case cowanol (7) [9].

Garcinia nervosa Miq. (syn. *G. andersonii* Hook.) is found particularly near water, its range being similar to that of *G. pyrifera* but extending to the Philippines [3].

Table 1. ^{13}C NMR chemical shifts for xanthenes 1 and 2 and the methylated derivatives of 2 and 3†

Carbon number	1	2	2-OMe ₄	3-OMe ₄
1	165.4*	162.7*	—	—
2	98.8	98.3	90.5	90.7
3	164.9*	162.5*	—	—
4	93.8	106.4	—	—
4a	156.3**	159.5	—	—
5	102.8	102.9	97.7	97.7
6	157.5**	155.1**	—	—
7	144.7	144.6	—	—
8	138.3	138.2	—	—
8a	112.0	111.8	—	—
9	182.7	183.1	—	—
9a	103.0	104.0	—	—
10a	156.6**	156.4**	—	—
1'	27.3	27.3	26.1	26.0
2'	124.8***	124.1***	124.1*	125.8*
3'	135.1	135.1	—	—
3'-Me	16.6	16.6	16.1	16.2
4'	40.2	40.4	39.6	39.8
5'	26.8	26.8	26.6	26.8
6'	125.2***	125.2***	123.9*	124.6*
7'	131.5	131.4****	—	—
7'(Me) ₂	17.7/25.8	17.7/25.8	17.6/25.7	17.5/25.5
1''	—	22.1	21.6	21.3**
2''	—	123.5	122.2*	124.0*
3''	—	131.5****	—	—
3''-Me	—	25.7	25.5	21.4**
3''-Me or CH ₂ OH	—	18.1	18.1	61.7
OMe	61.4	61.5	60.7/56.2/ 55.8/55.7	60.7/56.3/ 55.9/55.8

† Resonances in the same column with the same number of asterisks are interchangeable. Spectra of 1 and 2 were obtained at 62.5 MHz in $\text{Me}_2\text{CO}-d_6$ and those for the methylated xanthenes at 90.56 MHz in CDCl_3 .

Identical treatment of the stem bark gave a mixture of sitosterol and stigmasterol, 1 and a second xanthone which analysed for $C_{28}H_{32}O_6$. This last compound, which has been given the trivial name of nervosaxanthone, was assigned structure 8 on the basis of the following evidence.

Nervosaxanthone gave a UV spectrum for a 1,3,5,6-tetraoxygenated xanthone [4] and on acetylation gave a tetra-acetate indicating that all four were free hydroxy substituents. The 1H NMR spectrum revealed signals for two 3,3-dimethylallyl and one 1,1-dimethylallyl substituents, one of the former being placed at C-8 due to the deshielding of the Ar- CH_2 resonance to $\delta 4.09$ because of its position *peri* to the carbonyl. A single aromatic proton occurred at $\delta 7.22$, typical of H-7, leaving the other two prenyl units to occupy C-2 and C-4. The remaining problem, the relative placement of the other 3,3-dimethylallyl and the 1,1-dimethylallyl unit at C-2 and C-4, was resolved by preparation of the tri- and tetraacetates. A comparison of their 1H NMR spectra revealed that additional acetylation of C-1 caused appreciable shifts in one of the methyl groups and the vinylic methine proton of the 1,1-dimethylallyl group which must therefore be placed at C-2. On this basis nervosaxanthone must be 8.

The final species to be examined, *Garcinia polyantha* Oliv. (syn. *G. barteri* Oliv., *G. chevalieri* Engl.), is a tree of the rain forest canopy found throughout west Africa [10]. From the stem bark extracts three compounds were obtained, a xanthone ($C_{23}H_{24}O_6$), and the benzophenones xanthochymol and isoxanthochymol which were identified by direct comparison to authentic material [11]. Analysis of the UV and 1H NMR spectra of the xanthone revealed a 1,3,5,6-oxygenated compound substituted at C-2 and C-4 with 1,1-dimethylallyl units, with one of those units cyclized onto the C-3 hydroxyl function. These data comply with the two known compounds rheediaxanthone-B (9) and isorheediaxanthone-B (10). The identity of the compound as 10 was confirmed by a comparison of 1H spectra (250 MHz) of the isolated compound and its diacetate with authentic material of 10 and the diacetate 11. Comprehensive 1H NMR data on 10 and 11 have not been previously published and it is considered worthwhile to do so here (Table 2) as these

data readily allow differentiation between the two isomers.

These findings make a useful additional contribution to the development of a chemotaxonomic profile for *Garcinia* [2]. According to Engler [12] *G. polyantha* is placed in *Garcinia* section *Rheediopsis* together with *G. ovalifolia* and *G. staudtii*. This group of taxa is characterized by (a) the production of 1,3,5,6-oxygenated xanthenes carrying prenyl substituents at C-2 and C-4 and (b) by the presence of xanthochymol. This section also shows close biochemical ties to the genus *Rheediopsis* which has been the source of some of the same and other similar xanthenes [13-15]. *Garcinia pyrifera* was unassigned by Engler [12] but clearly shows a close biochemical similarity to investigated species of the section *Oxycarpus*, *G. cowa* and *G. rubra*, all three producing 7-methoxy-1,3,6-trihydroxyxanthenes with a geranyl substituent at C-8.

Garcinia nervosa, under the name *G. andersonii*, was assigned by Engler [12] to the section *Xanthochymus* which includes species from south east Asia, India and west Africa. Previous work on five other species has not shown a cohesive biochemical profile in either xanthone or benzophenone production but all five do produce flavanone/flavone dimers. The addition of data for *G. nervosa* does nothing to resolve the complex picture in this section; the presence of 1,3,5,6-substituted xanthenes (cf. nervosaxanthone) had been reported from one other species, *G. densivenia* [2, 14], but this is the first record of 1,3,5,6-substitution in Asian taxa of this section. Furthermore no biflavonoids were detected in this present investigation.

In the light of the chemical homogeneity shown by the taxa in some of Engler's sections of *Garcinia*, notably *Rheediopsis* and *Oxycarpus*, the application of xanthone markers in the genus seems to hold some taxonomic promise. However, if this is the case then the chemical data points out the need to look critically at section *Xanthochymus*.

EXPERIMENTAL

Plant material. Stem barks of *G. pyrifera* and *G. nervosa* were collected in the Kuala Lompat study area of the Krau Game

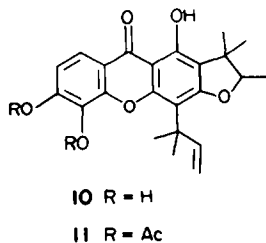
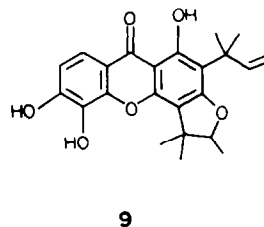
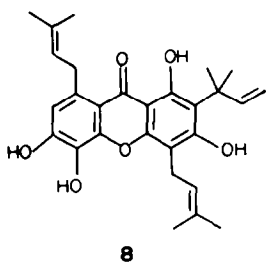


Table 2. ^1H NMR chemical shifts for rheediaxanthone B (9), isorheediaxanthone B (10) and isorheediaxanthone B diacetate (11)

Signal	9	10	11
OH-1 s	14.08	13.24	13.10
H-7 d	6.93 (8.8)	6.94 (8.7)	7.21 (8.7)
H-8 d	7.77 (8.8)	7.68 (8.7)	8.13 (8.7)
Furan ring			
H-2' g	4.45 (6.6)	4.45 (6.3)	4.43 (6.2)
2'-Me d	1.39 (6.6)	1.39 (6.3)	1.36 (6.2)
3'-(Me) ₂ s	1.57	1.60	1.63
s	1.59	1.60	1.63
Open side-chain			
1''-Me s	1.31	1.26	1.26
1''-Me s	1.56	1.50	1.48
2''-H dd	6.35 (17.4, 10.7)	6.66 (17.8, 10.5)	6.18–6.29*
3''-H	4.95 (17.4, 1.4)	5.24 (17.8, 1.4)	4.90*
3''-H dd	4.89 (10.7, 1.4)	5.08 (10.5, 1.4)	4.82–4.86*

Spectra run at 250 MHz in CDCl_3 . J values in parentheses.

*Coupling not first order.

Reserve, west Malaysia and vouchers are deposited at the herbarium of the Universiti Kebangsaan Malaysia. *Garcinia polyantha* was collected in the Korup National Park in Cameroon and a voucher sample has been deposited at the Herbarium of the Missouri Botanic Garden.

Extraction of stem barks. Ground stem barks were extracted with petrol (bp 40–60°) and then EtOAc (*G. pyrifera* 500 g; *G. nervosa* 600 g; *G. polyantha* 250 g). In each case TLC examination of concn petrol and EtOAc extracts showed identical profiles of compounds and these were bulked for subsequent analysis.

Isolation of compounds from *G. pyrifera*. The concd extract was subjected to CC over silica gel eluting with petrol (bp 60–80°) and then petrol containing increasing amounts of EtOAc. Elution with 3% EtOAc gave crude β -amyrin which was purified by circular prep. TLC using the same solvent to give 250 mg pure compound (identical in all respects, IR, ^1H NMR, MS, OR, mmp) with an authentic sample. Elution with 4% EtOAc gave a mixture from which 2 (400 mg) ppt on standing. The supernatant was subjected to circular prep. TLC using silica gel (solvent, toluene–EtOAc–AcOH, 95:5:0.5) and gave oleanolic aldehyde (80 mg). Further elution with 5% EtOAc gave a sitosterol/stigmasterol mixture and with 10% EtOAc yielded 1 (350 mg). Finally elution with 20% EtOAc gave a yellow amorphous solid from which 3 (48 mg) was obtained after circular prep. TLC (solvent, toluene–EtOAc–AcOH, 5:4:1).

Oleanolic aldehyde. Amorphous solid, $[\alpha]_D^{25} + 56^\circ$ (c 0.1; CHCl_3) (lit. [16] + 71°). Found: $[\text{M}]^+ 440.3637$; $\text{C}_{30}\text{H}_{48}\text{O}_2$ requires 440.3654. IR ν_{max} cm^{-1} : 3400, 1725, 1460. ^1H NMR (90 MHz, CDCl_3): δ 0.78–1.09 (7 s, 7 × Me), 3.20 (1H, dd, $J = 10, 6$ Hz, H-3), 5.31 (1H, br t, $J = 4$ Hz, H-12), 9.32 (1H, s, 17-CHO). MS m/z rel. int.: 440 $[\text{M}]^+$ (18), 411 $[\text{M} - \text{CHO}]^+$ (51), 232 (57), 207 (50), 202 (100). Acetylation with Ac_2O in pyridine yielded the corresponding 3 β -acetate, identical in all respects with published data [17].

Rubraxanthone (1). Yellow prisms from petrol–EtOAc, mp 210° (lit. [6] 205–206°). Found: $[\text{M}]^+ 410.1713$; $\text{C}_{24}\text{H}_{26}\text{O}_6$ requires 410.1729. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 242, 253, 310, 348; (+NaOH) 265, 296, 357; (+ AlCl_3) 260, 341, 390; (+NaOAc) 290, 354. IR ν_{max} cm^{-1} : 3450, 1655, 1610, 1580. ^1H NMR (250 MHz,

$\text{Me}_2\text{CO}-d_6$: δ 1.53, 1.57, 1.83 (3 × 3H, 3 × s, 3 × Me), 3.80 (3H, s, 7-OMe), 4.12 (2H, d, $J = 7$ Hz, CH_2 –Ar), 5.05 (1H, m, H-6'), 5.29 (1H, t, $J = 7$ Hz, H-2'), 6.19, 6.29 (2H, ABq, $J = 2$ Hz, H-2 and H-4), 6.81 (1H, s, H-5), 13.38 (1H, s, 1-OH). ^{13}C NMR: see Table 1. MS m/z (rel. int.): 410 $[\text{M}]^+$ (47), 341 $[\text{M} - \text{C}_5\text{H}_9]^+$ (100), 299 (32)—ion 4, 285 (14).

Isocowanin (2). Yellow clusters from petrol–EtOAc, mp 160°. Found: $[\text{M}]^+ 478.2339$; $\text{C}_{29}\text{H}_{34}\text{O}_6$ requires 478.2355. UV λ_{max} nm: 239, 256, 313, 352. IR ν_{max} cm^{-1} : 3400, 1650, 1602, 1510. ^1H NMR (90 MHz, $\text{Me}_2\text{CO}-d_6$): δ 1.64, 1.82, 1.87 (5 × Me), 3.45 (2H, d, $J = 7$ Hz, CH_2 –1'), 3.80 (3H, s, 7-OMe), 4.12 (2H, d, $J = 8$ Hz, CH_2 –1'), 5.02 (1H, m, CH-6'), 5.29 (2 × 1H, 2 × t, CH-2' and CH-2''), 6.26 (1H, s, H-2), 6.87 (1H, s, H-5), 13.40 (1H, s, 1-OH). ^{13}C NMR: see Table 1. MS m/z (rel. int.): 478 $[\text{M}]^+$ (62), 409 (100), 367 (13), 355 (16). Compound 2 (60 mg) was dissolved in dry Me_2CO (60 ml) and MeI (3 ml) and anhydrous K_2CO_3 (2 g) added. The mixture was refluxed for 24 hr with addition of further MeI and K_2CO_3 and then cooled and filtered. Normal work-up gave the 1,3,6-trimethyl ether of 2 as a white amorphous solid. UV λ_{max} nm: 250, 300, 340 (no change with NaOH). ^1H NMR (90 MHz, CDCl_3): δ 1.54, 1.60, 1.68, 1.82, 1.89 (5 × C-Me), 1.90–2.15 (4H, m, CH_2 –4', CH_2 –5'), 3.50 (2H, CH_2 –1'), 3.78, 3.95, 3.95, 3.99 (4 × OMe), 4.13 (2H, CH_2 –1'), 5.02 (1H, CH-6'), 5.28 (2H, CH-2' and CH-2''), 6.37 (1H, H-2), 6.73 (1H, H-5). ^{13}C NMR: see Table 1.

Isocowanol (3). Amorphous solid. Found: $[\text{M}]^+ 494.2308$; $\text{C}_{29}\text{H}_{34}\text{O}_7$ requires 494.2304. UV λ_{max} nm: 240, 254, 312, 350. IR ν_{max} cm^{-1} : 3300, 1650, 1605, 1580. ^1H NMR (90 MHz, $\text{Me}_2\text{CO}-d_6$): δ 1.57, 1.76, 1.83 (12H, 4 × Me), 1.90–2.20 (4H, m, CH_2 –4', CH_2 –5'), 3.55 (2H, d, $J = 8$ Hz, CH_2 –1'), 3.80 (3H, s, 7-OMe), 4.12 (2H, d, $J = 8$ Hz, CH_2 –1'), 4.40 (2H, br s, 3''- CH_2OH), 5.02 (1H, m, CH-6'), 5.31 (2H, 2 × t, CH-2' and CH-2''), 6.25 (1H, s, H-2), 6.95 (1H, s, H-5), 13.41 (1H, s, OH-1). MS m/z (rel. int.): 494 $[\text{M}]^+$ (96), 479 $[\text{M} - \text{Me}]^+$ (11), 476 $[\text{M} - \text{H}_2\text{O}]^+$ (16), 461 (24), 425 (100), 407 (80), 383 (11). Methylation of 3 (10 mg) by the method described above gave the trimethyl ether. ^1H NMR (90 MHz, CDCl_3): δ 1.50, 1.50, 1.79, 1.89 (4 × C-Me), 3.50 (2H, CH_2 –1'), 3.81, 3.88, 3.95, 3.95 (4 × OMe), 4.12 (2H, CH_2 –1'), 4.40 (2H, 3''- CH_2OH), 5.00 (1H, CH-6'), 5.27 (2H, CH-2' and CH-2''), 6.57 (1H, H-2), 7.07 (1H, H-5).

Isolation of compounds from G. nervosa. CC of the concd extract over silica gel followed the same procedure as for *G. pyrifera*. From the eluate collected using 10% EtOAc 1 (23 mg) was obtained and identified by comparison with material from *G. pyrifera*. Elution with 15% EtOAc gave **8** as an impure brown solid which was then purified by circular prep. TLC on silica gel (solvent, toluene–EtOAc–AcOH; 70:30:3) to give a yield of 12 mg.

Nervosaxanthone (8). Amorphous. Found: $[M]^+$ 464.2170; $C_{28}H_{32}O_6$ requires 464.2199. UV λ_{max} nm: 230, 258, 283, 342. IR ν_{max} cm^{-1} : 3600–3100, 1610, 1580, 1500. 1H NMR (250 MHz, Me_2CO-d_6): δ 1.52 (6H, s, 1'-Me₂), 1.66, 1.67, 1.78, 1.79 (4 × 3H, 4 × s, 3''-Me₂, 3'''-Me₂), 3.46 (2H, d, $J = 6.4$ Hz, CH₂-1''), 4.09 (2H, d, $J = 6.1$ Hz, CH₂-1''), 4.98 (1H, dd, $J = 10.0, 1.5$ Hz, H-3'), 5.01 (1H, dd, $J = 18.0, 1.5$ Hz, H-3'), 5.10 (2H, m, CH-2' and CH-2'''), 6.30 (1H, dd, $J = 18.0, 10.0$ Hz, H-2'), 7.22 (1H, s, H-7), 13.52 (1H, s, OH-1). MS m/z (rel. int.): 464 $[M]^+$ (96), 449 (19), 396 (42), 393 (36), 381 (32), 367 (100). Acetylation of **8** with Ac_2O in pyridine at 60° overnight followed by normal workup gave a mixture of compounds which were separated by circular prep. TLC over silica gel (solvent, toluene–EtOAc–AcOH, 19:1:0.1). The major compound was identified as the 3,5,6-triacetate; 1H NMR (250 MHz, Me_2CO-d_6): δ 1.51, 1.52, 1.66, 1.67, 1.77, 1.79 (6 × Me), 2.03, 2.04, 2.05 (3 × COMe), 3.40, 4.19, (2 × CH₂), 5.03 (2H) and 6.23 (H-3' and H-2'), 7.49 (H-7), 13.62 (OH-1). The minor compound was identified as the 1,3,5,6-tetraacetate; 1H NMR (250 MHz, Me_2CO-d_6): δ 1.43, 1.51, 1.65, 1.67, 1.75, 1.78 (6 × Me), 2.03, 2.04, 2.05, 2.06 (4 × COMe), 3.37, 4.00 (2 × CH₂), 5.04, 5.10, 6.00 (H-3' and H-2') 7.69 (H-7).

Isolation of compounds from G. polyantha. Identical treatment of extracts as above led to the elution of **10** (20 mg) from a silica gel column with 5% EtOAc. Further elution with 10% EtOAc yielded xanthochymol and 20% EtOAc gave isoxanthochymol. The benzophenones were both purified by circular prep. TLC using toluene–EtOAc–AcOH (90:9:1) as solvent, final yields being xanthochymol (300 mg) and isoxanthochymol (104 mg). Both compounds were confirmed by direct comparison with authentic samples [11].

Isorheediaxanthone-B (10). Yellow clusters from petrol, mp 218° (lit. [15] 212–213°), $[\alpha]_D^{25} + 25^\circ$ (c 0.1; Me_2CO) (lit. [15] + 16°). Found: $[M]^+$ 396.1561; $C_{23}H_{24}O_6$ requires 396.1573. UV, IR, MS in agreement with published data [15]. 1H NMR: see Table 2. Acetylation (method as for **8**) gave a mixture of the di- and triacetate. Separation of the former by circular prep. TLC (solvent; toluene–EtOAc–AcOH, 90:9:1) gave the diacetate as an amorphous solid; 1H NMR: see Table 2; UV, IR, TLC identical to an authentic sample.

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